Graphitization of small carbonate samples for palaeoceanographic research at the Godwin Radiocarbon Laboratory, University of Cambridge

E. Freeman[1], L.C. Skinner[1], R. Reimer[2], A. Scrivner[1], S. Fallon[3]

1. Godwin laboratory for Palaeoclimate Research, Department of Earth Sciences, University of Cambridge, CB2 3EQ, UK.
2. CHRONO centre, Queen's University Belfast, Belfast, BT9 6AX, UK.
3. Research School of Earth Sciences, The Australian National University, Canberra ACT 0200, Australia

A new radiocarbon preparation facility was set up in 2010 at the Godwin Laboratory for Palaeoclimate Research, at the University of Cambridge. Samples are graphitized via hydrogen reduction on an iron powder catalyst before being sent to the Chrono Centre, Belfast, or the Australian National University for accelerator mass spectrometry (AMS) analysis. The experimental set-up and procedure have recently been developed to investigate the potential for running small samples of foraminiferal carbonate. By analysing background values of samples ranging from 0.04-0.6mgC along with similar sized secondary standards, the set-up and experimental procedures were optimised for small samples. 'Background' modern radiocarbon contamination has been minimised through careful selection of iron powder, and graphitization has been optimised through the use of 'small volume' reactors, allowing samples containing as little as 0.08mgC to be graphitized and accurately dated. Graphitization efficiency/fractionation is found not to be the main limitation on the analysis of samples smaller than 0.07mgC, which rather depends primarily on AMS machine dependent ion beam optics, suggesting further improvements in small sample analysis might yet be achieved with our methodology.

Introduction

Significant advances in the graphitization and AMS-dating of small samples have been made in recent years (e.g. Santos et al., 2007; Delque-Kolic et al., 2013), but only one of these studies have been specifically targeted for small carbonate samples used in palaeoceanograpic research (Walter et al., 2015).

Carbonate samples, primarily foraminifer shells, are graphitized in the Godwin Radiocarbon laboratory and pressed into cathode targets before being sent for accelerator mass spectrometry (AMS) analysis. The laboratory was initially set-up and developed to run samples containing ~0.6mgC (approximately 6mg of carbonate), but demand for running smaller samples allowing, in particular, dating of foraminifera from deep-sea cores where abundances are low has led us to adapt the process to run smaller samples.

In order to do this the background contamination must be accurately determined and reduced. The contamination in our methodology is predominantly modern carbon, with high $^{14}C/^{12}C$, such that older and smaller samples are most affected. Fractionation of isotopes during the graphitization process must also be minimised for samples of all sizes and ages, primarily by ensuring the reduction reaction goes to completion.

The graphitization process is complex and involves several reactions that are sensitive to temperature, pressure, the initial ratio of H_2:CO_2, water content, the catalyst and various other factors. Since a high yield of graphite must be produced in order to minimise fractionation of the carbon isotopes, all of these parameters need to be optimised. Here the yield, fractionation (using both $\delta^{13}C$ and $\Delta^{14}C$ measurements) and contamination are used to optimise the set-up and procedures in order to produce accurate radiocarbon measurement on small samples of carbonate.

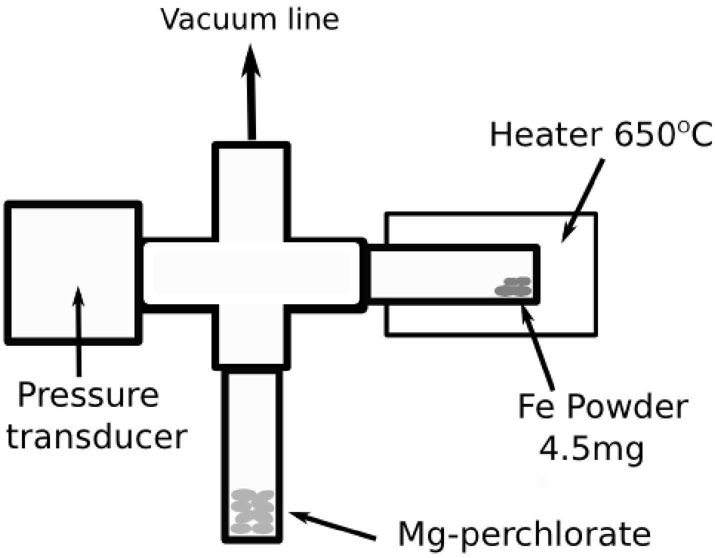
Both the background contamination and the amount of fractionation during graphitizing were minimised by changing various aspects of the process for both full size and small samples. The new set up was then tested with the secondary standard IAEA-C8 and with a large carbonate sample of approximately 20kyr age that was spilt into small samples.

Methods

Laboratory set-up and experimental procedure

The new Godwin radiocarbon preparation facility was set up based on that used at ANU, which is in turn based on the Irvine lab design (Santos et al., 2007). The laboratory contains one vacuum line with 11 small volume reactors (~4.0cm^3) fitted with 0-15psi pressure transducers and two 50mm quartz tubes (with 4mm internal diameter). Each reactor is preloaded with iron powder and magnesium perchlorate [Figure 1] and flushed with hydrogen several times. One atmosphere of hydrogen is added to the reactors that are then heated for 90mins at 450°C to precondition the line immediately prior to graphitizing. This removes much of the carbon contamination and improves the effectiveness of the iron powder as a catalyst. For carbonate samples, CO_2 is produced by reacting the sample with phosphoric acid in an evacuated double-septum vial at 80°C for a minimum of 1hr. The carbonate is loaded into the vial which is then evacuated before phosphoric acid is injected using a single needle. The CO_2 is then introduced into the line via a needle and water vapour is removed using an ethanol cold trap at -80°C. The CO_2 is transferred into a reactor and hydrogen added to give the desired H_2:CO_2 [see Discussion]. Each reactor is then heated at 650°C for at least 2.5 hours, until the reactor pressure reaches a minimum. Finally, the graphite is removed from the line and pressed into cathode targets to be sent to the AMS laboratory along with backgrounds and standards. The carbonate backgrounds and secondary standard IAEA-C2 are graphitized in the same way as the samples. Primary standard OXII and additional secondary standards IAEA-C7 and IAEA-C8 are heated with copper oxide and silver at 900°C for 300mins in sealed quartz tubes to produce CO_2 which is then introduced to the line and split into individual samples.

Figure 1: Schematic diagram of the reactor set-up.



Isotope Measurements

Once graphitised, samples were either prepared for stable isotope analysis or for radiocarbon dating at an AMS facility. Samples for stable isotope analysis were ground into a fine powder and transferred into tin capsules in the Godwin Laboratory, University of Cambridge. These were then run on a Costech Elemental Analyser attached to a Thermo DELTA V mass spectrometer in continuous flow mode along with IAEA reference standards. The precision of analyses is better than 0.1‰ for $^{13}C/^{12}C$.

Samples for radiocarbon analysis were pressed into NEC aluminium cathode targets before being sent to the Chrono Centre, Belfast, or on one occasion the AMS facility at ANU. Each set of samples was run with primary and secondary standards along with calcite blanks (Icelandic Spar) produced in our laboratory via the methods described above.

Yield

The yield is calculated based on the pressure in each reactor, using the equation:

$$Yield = \frac{(pH_2 + pCO_2)_{initial} - Residual\ pressure}{3 \times pCO_{2,initial}}$$

where $pH_{2\ initial}$ and $pCO_{2\ initial}$ are the initial pressures of H_2 and CO_2 respectively, and residual pressure is the final pressure at the end of heating.

Optimising the process

Three different iron powders were tested; Analar Normapur, Alfa Aesar-325 mesh and Fisher Fe. For each, the amount was kept constant at 4.5-5mg and the experimental procedure was identical. The amount of hydrogen added to the CO_2 was varied to find the optimal H_2:CO_2. The temperature and duration of heating were also investigated to maximise the yield and the rate of reaction. Each of these variables was optimised using the yield, $\delta^{13}C$ and $\Delta^{14}C$ measurements to ensure the reaction was complete, with minimal contamination, and within the shortest time. A standard and a carbonate sample of approximately 20kyr age were then used to test the new set-up for a range of sample sizes.

Results and Discussion

Iron Powder

Samples of radiocarbon ‘free’ Icelandic Spar calcite were graphitised using three different iron powders as the catalyst. For each, a range of sample sizes were graphitized and the yield determined to assess the completeness of the reaction and hence the potential for fractionation. The samples were then sent to the AMS laboratory to be dated in order to determine the background contamination levels. Figure 2 shows the variation in yield for the different iron powders over a range of sample sizes. The yield was high, over 98%, for all of the iron powders for samples ranging from 0.04mgC to 0.7mgC and often greater than 100% (see section: H_2:CO_2). There is a fair amount of scatter in the yields, especially for the smaller samples, but none of the iron powders had a significantly better yield than the others. Figure 3 shows the background $^{14}C/^{12}C$ data for a range of sample sizes using each of the three iron powders. This clearly shows that the background varies significantly depending on the iron powder used, with Alfa Aesar-325 leading to the highest background values and Analar Normapur being associated with the lowest background values. A lower background means that samples can be smaller and/or older before they are significantly affected by the contamination. Background (i.e. ‘radiocarbon-dead’) samples smaller than 0.3mgC start to be significantly affected by the contamination when Alfa Aesar-325 is used, whereas only those smaller than around 0.07mgC are affected when Analar Normapur is used. For this reason, Analar Normapur is now used as the catalyst for all samples.

The amount of catalyst is kept constant regardless of the size of the sample. This has the advantage of keeping the contamination constant and the current beam as high as possible for the small samples (Turnbull et al., 2010).

Figure 2: Yields resulting from using different iron powders to catalyse the graphitising reaction, for a range of sample sizes. The grey bar indicates the region where samples cannot be accurately dated.

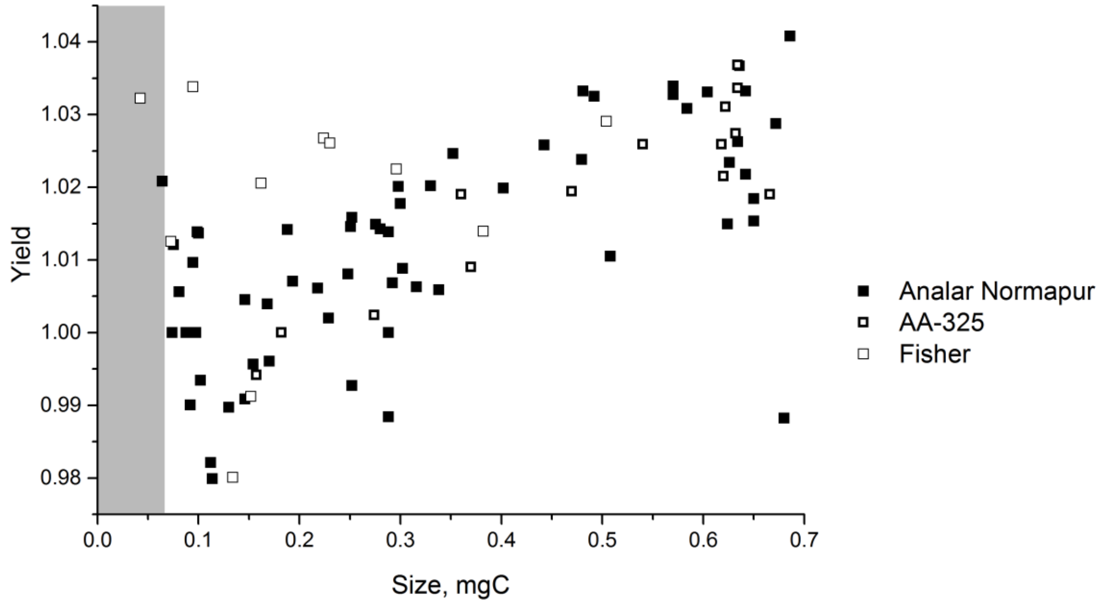
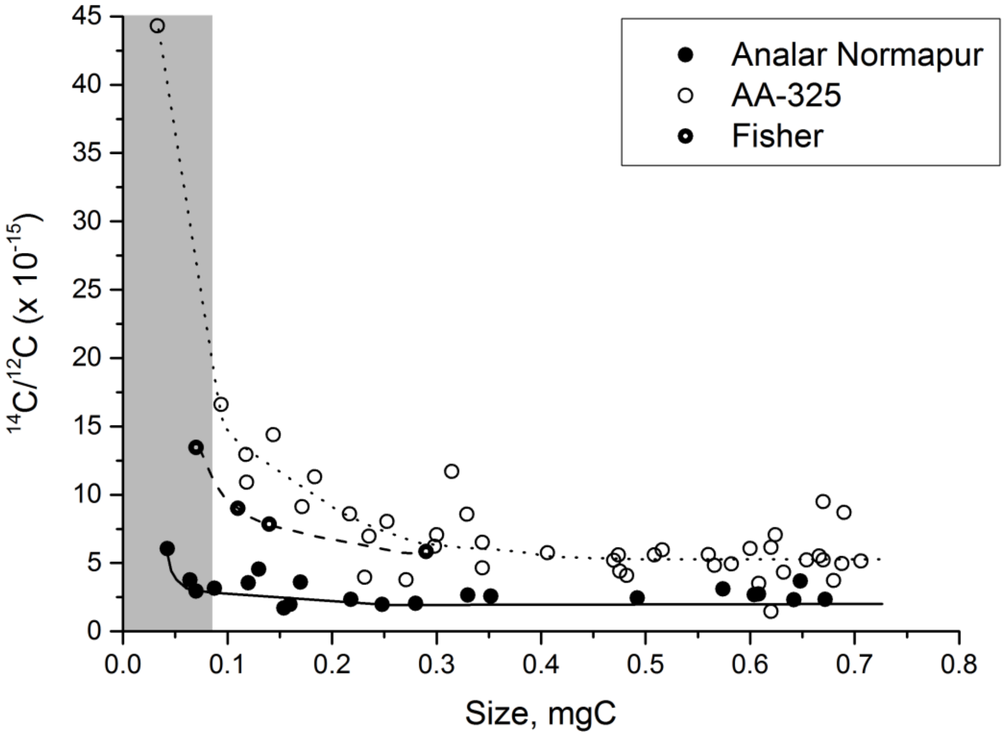


Figure 3: Background measurements using different iron powders, for a range of sample sizes. The grey bar indicates the region where samples cannot be accurately dated.



Temperature and Duration of Heating

The graphitization reaction is highly sensitive to temperature, with the yield and the reaction time both being affected. The optimal temperature will allow the reaction to have a high yield in a short amount of time. The reactor pressure can be used as an indicator of the reaction completeness as the reaction involves two gases, CO_2 and H_2, being converted into a solid, graphite. Water vapour is also produced but is removed by the magnesium perchlorate. Figure 4 shows the reactor pressure for a series of reactors containing different initial amounts of CO_2 over the course of the graphitization at both 550°C and 650°C. The pressure initially increases as the heaters are switched on, but quickly decreases as the reaction starts to occur. For samples heated at 550°C, the decrease is much slower than for those heated at 650°C and, for the larger samples, the reaction at

550°C is still not complete after 3hrs. For samples heated at 650°C the reaction is complete within 1.5hrs for all sample sizes. Figure 5 shows the effect of increasing the temperature during the reaction. Samples were heated at 550°C for just over 3hrs before the temperature was increased to 650°C. On increasing the temperature, the rate of reaction immediately increases and the reaction was completed after a further 40mins, for the largest sample. Graphitizing at higher temperatures can cause the graphite to sinter and whilst this does start to occur in our reactors at 650°C, it is insufficient to prevent samples from being pressed effectively and does not affect the AMS results.

Whilst many radiocarbon laboratories use lower temperatures for smaller samples, (e.g. Santos et al., 2007; Delque-Kolic et al., 2013), high yields and low fractionation have been achieved during these experiments for samples as small as 0.04mgC at 650°C thus demonstrating no need to lower the temperature. This could be a result of very effective water removal (Turnbull et al., 2010).

Figure 4: Reactor pressure over the course of graphitizing at either 550°C (dashed) or 650°C (solid), for various sample sizes.

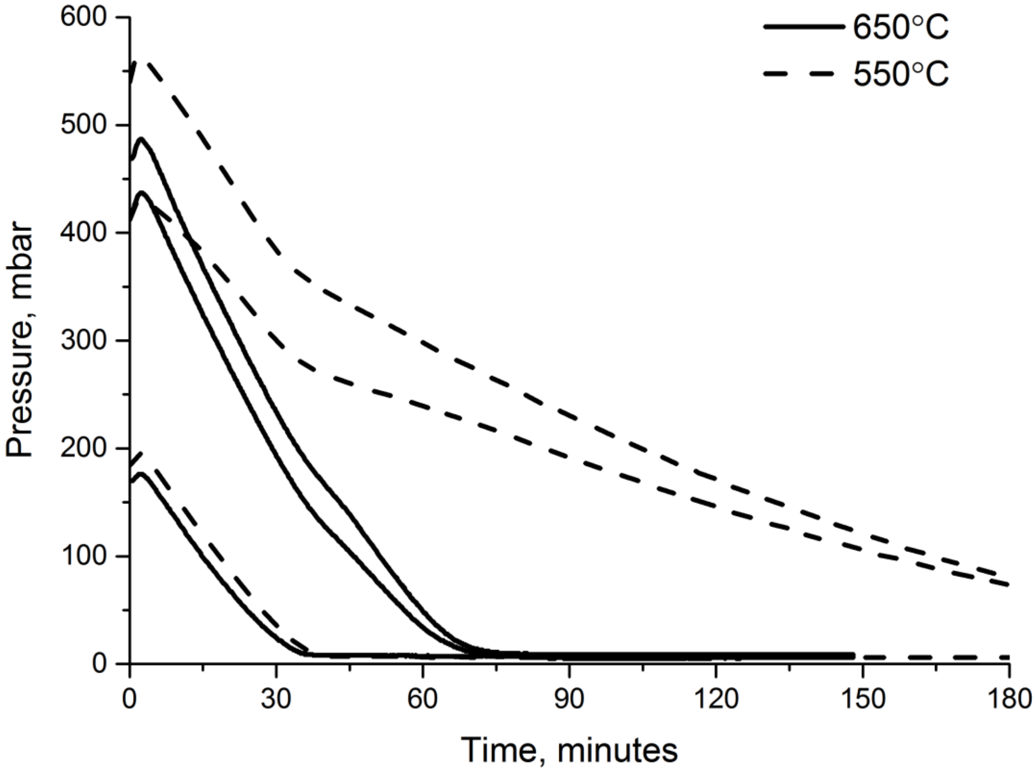
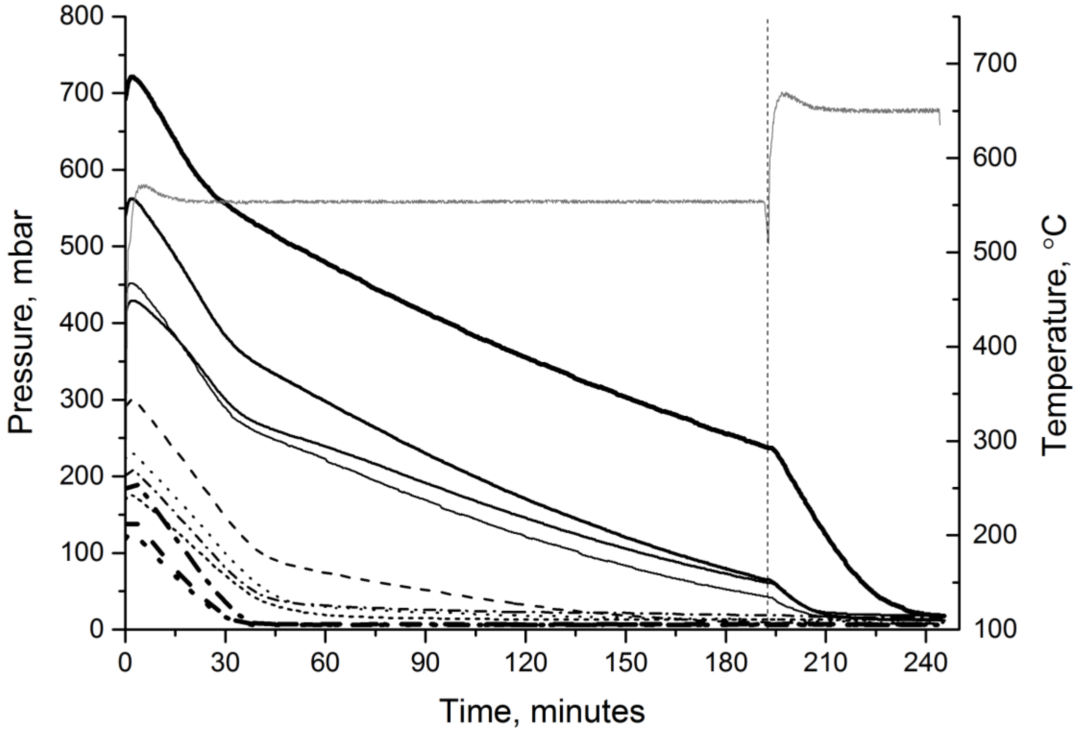


Figure 5: Reactor pressure (black lines) over time when heated initially at 550°C, then at 650°C. Each line represents a different reactor. The reactor temperature (grey line) is also shown.



Water removal

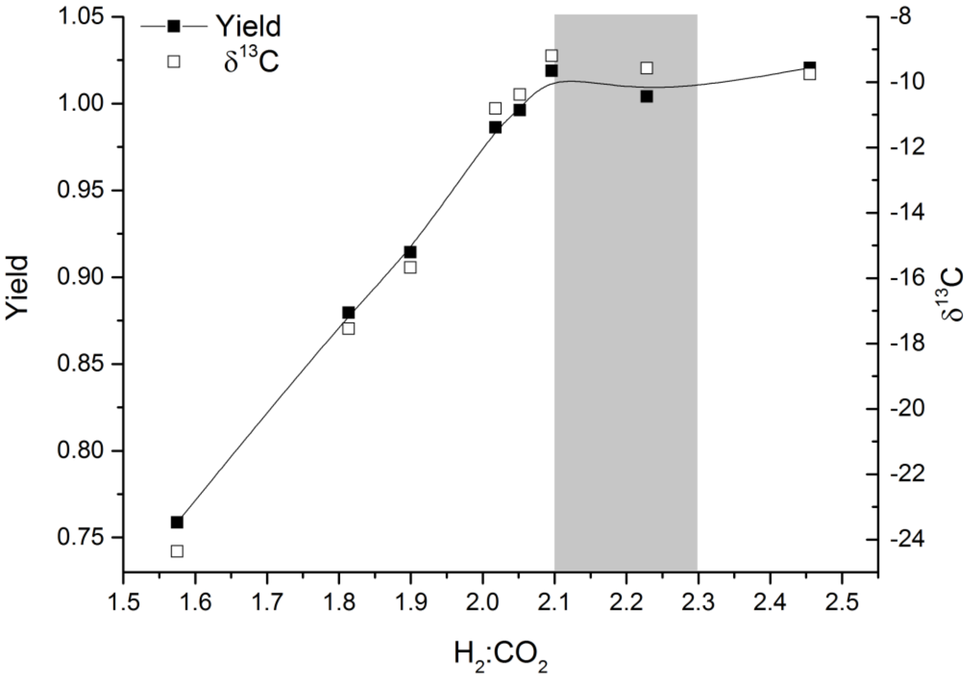
Magnesium perchlorate ($Mg(ClO_4)_2$) flakes are used to chemically remove any water, following Santos et al. (2004). Around 40mg of magnesium perchlorate flakes are preloaded in the reactors prior to preconditioning. These remove water during both the preconditioning and during the graphitization reaction. The water removal appears to be highly effective, so this part of the set-up remained unaltered.

H_2:CO_2

For each reactor, the pressure of hydrogen added to the line is twice the pressure of CO_2 in the reactor. The CO_2 is frozen down and the reactor opened to allow H_2 in (this is done as rapidly as possible in order to minimise excess condensation and over-pressurization of H_2 in the reactors). This results in a ratio of H_2:CO_2 in the reactor of 2.1:1 to 2.3:1, depending on the size of the CO_2

sample frozen down. For larger samples, the ratio is at the higher end and the yield is typically greater than one, indicating that more H_2 is used in the reaction than expected from the stoichiometry of the reaction. This could be attributed to the formation of a small amount of CH_4 or CO (Rinyu et al., 2007), however the lack of any deviation from the expected $\delta^{13}C$ and $\Delta^{14}C$ values for the larger samples indicate that no significant fractionation takes place (Figure 6). If additional carbon bearing products were produced fractionation would be expected. Alternatively, hydrogen molecules may be adsorbed onto the graphite. Lower H_2:CO_2 ratios were also tested but the yield dropped off rapidly and fractionation was observed (Figure 6).

Figure 6 : Yield (solid squares) and $\delta^{13}C$ (open squares) for various H_2:CO_2 ratios. The shaded region represents the typical range of H_2:CO_2 values used.

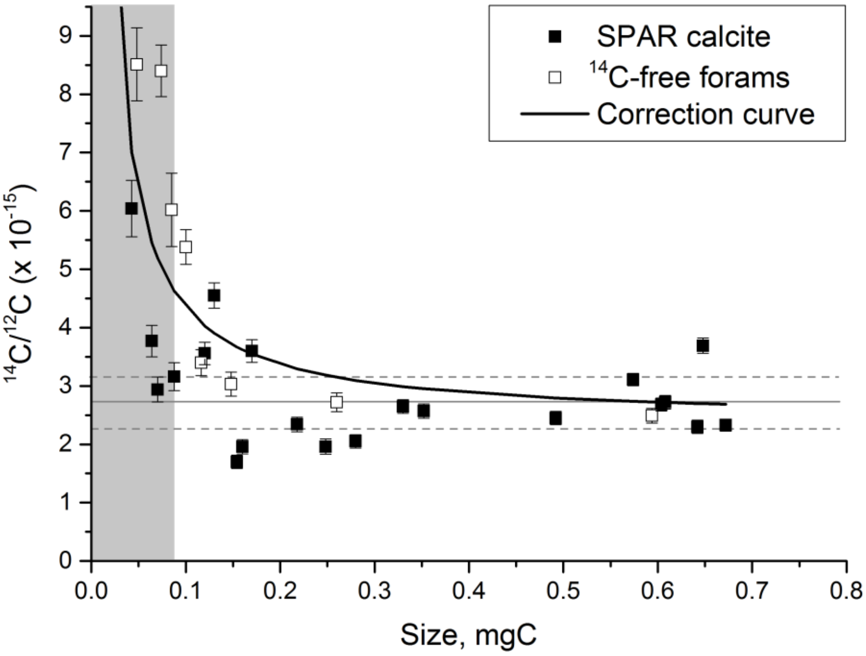


Size corrections

Background values for the new set up were determined using both Spar calcite and ‘radiocarbon-dead’ planktonic foraminifera (from Marine Isotope Stage 6; >130 ka). The small samples of ‘radiocarbon-dead’ planktonic foraminifera were individually weighed out and processed rather than being split on the line so that the background represents that of our sample process as closely as possible. The constant background contamination has an inverse mass relationship that becomes significant for background samples smaller than around 0.3mgC and particularly important for those less than 0.07mgC. A correction is therefore applied of the form $y(x_i) = a\frac{1}{x_i} + b$, where x is the mass of the sample (Figure 7). The constant coefficient a is 0.1958e^{-15}, determined using a least squares minimisation and b is calculated using a full size background sample for each wheel run at the AMS facility. Typically b is around 2.5e^{-15}, with an error of 25%, corresponding to 0.3-1.3μg of modern carbon contamination.

Figure 7: Background values for Spar calcite (solid squares) and ‘radiocarbon-dead’ planktonic foraminifer samples (open squares) graphitized using Analar Normapur iron powder. The solid line represents the size dependent background correction. The grey bar indicates the region where samples cannot be

accurately dated.



Testing the new set-up

Once the graphitization process had been refined, a series of samples were run in order to assess the size range over which accurate radiocarbon dates could be measured. A secondary standard was used, IAEA-C8, which has a known age of 15,224±91yrs, and a $\delta^{13}C$ value of -18.31‰ (Le Clercq et al., 1998). Figure 8 shows the $\delta^{13}C$ and radiocarbon ages obtained on samples from 0.04 to 0.7mgC. The current beams were >40µA for the largest samples but dropped to 6-10 µA for the smallest samples. Samples <0.07mgC could not be measured accurately on the AMS, as indicated by the large deviations in $\delta^{13}C$ measured by AMS that are not present in the graphite $\delta^{13}C$ values measured ‘off-line’ in the Godwin laboratory. The large deviations in radiocarbon activity and $\delta^{13}C$ are therefore not due to fractionation during graphitization, and instead are most likely due to the ion optics that become particularly important when the beam current is low. Deviations were found to be roughly of the same magnitude but in the opposite direction for similar sized samples run at the Chrono Centre versus at the ANU radiocarbon facility.

In order to assess the performance of the graphitization procedure for typical samples that would be analysed (i.e. relatively old carbonate), tests were run on a mix of IAEA-C2 and Icelandic Spar calcite, combined to give an age of around 20,300yrs. These tests indicated similar trends in radiocarbon and $\delta^{13}C$, with significant deviations in the AMS occurring for samples <0.07mgC (Figure 9). The smallest samples were up to 400yrs offset from the expected age of 15,224yrs for IAEA-C8 and 500yrs offset from the average age of 20,295yrs observed for the Spar-C2 mix. For this reason, samples smaller than 0.08mgC are not run at present. Having said this, the fractionation trends do initially look to be consistent at the different AMS facilities. If this is the case, by size matching samples of similar age, for example co-existing benthic and planktonic foraminifera, the age difference between the two samples could be determined accurately so long as they are measured at the same facility. This remains to be tested however.

Figure 8: Radiocarbon and stable carbon measurements for a range of sizes of IAEA-C8 samples analysed at various different locations. The grey bar indicates the region where samples cannot be accurately dated.

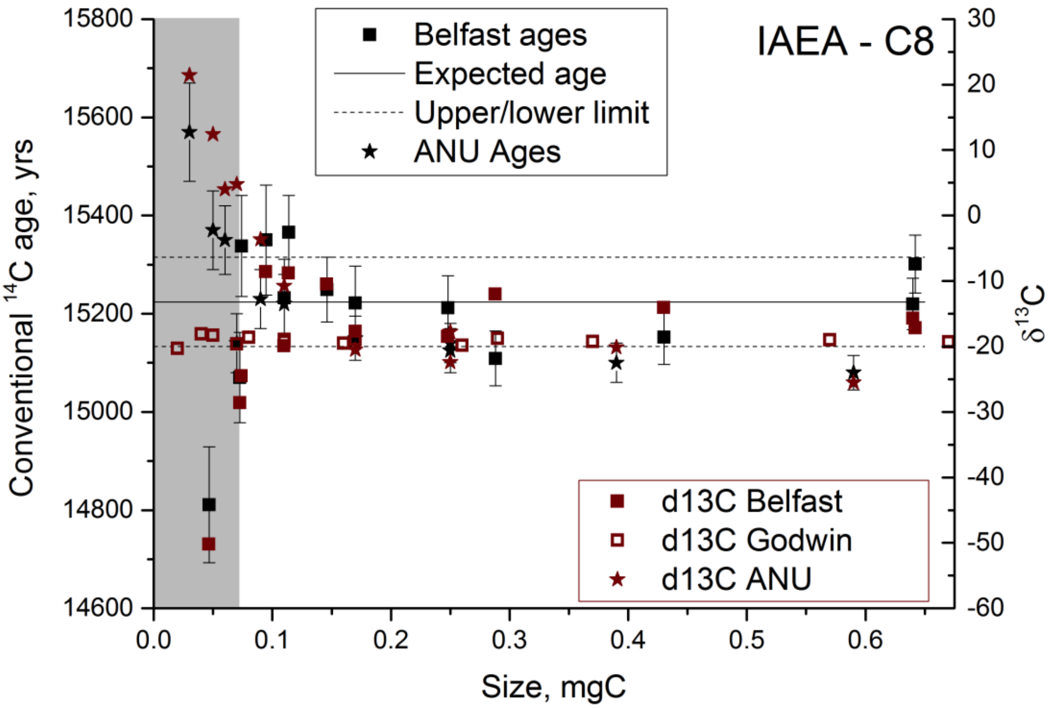
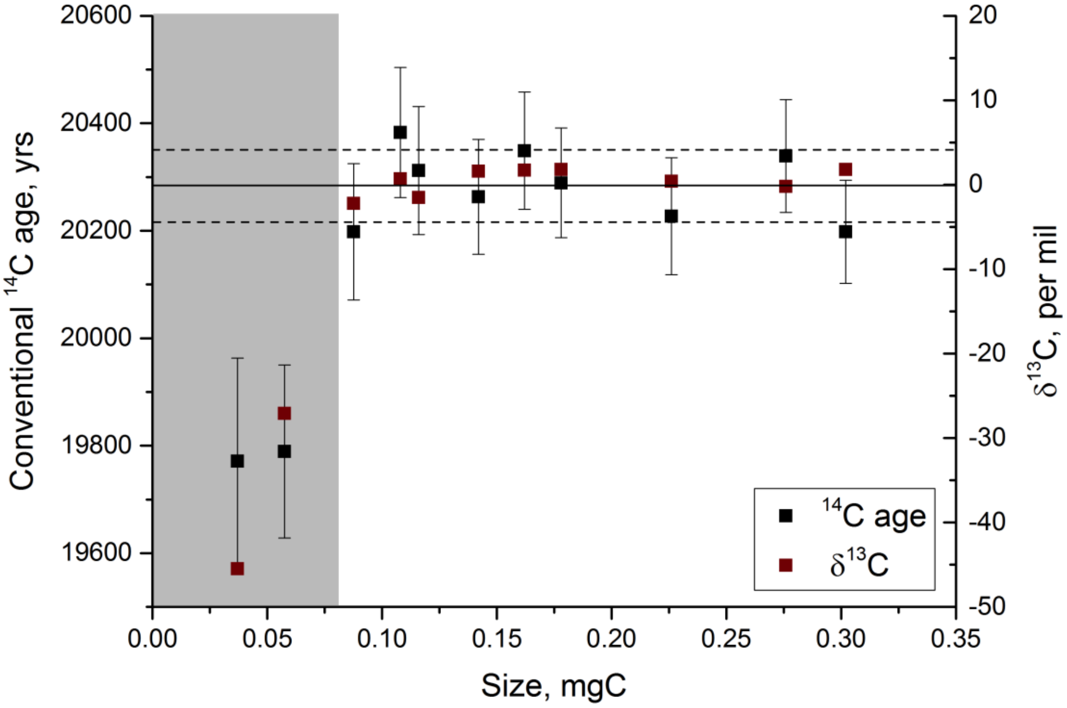


Figure 9: Radiocarbon and stable carbon measurements for a range of sizes of an approximately 20,300yr old sample, measured at the Chrono Centre, Belfast. The grey bar indicates the region where samples cannot be accurately dated.



Conclusions

The Godwin Radiocarbon laboratory has been set up at the University of Cambridge allowing the graphitization of carbonate and organic carbon samples, and the preparation of standards. The experimental procedure has been streamlined for small and relatively old carbonate samples (>20,000 years), and refined to maximise the yield, ensuring no fractionation occurs, while minimising the background radiocarbon levels. The reaction time has also been reduced. Standards have been used to show that samples containing 0.08-0.7mg of carbon, with a fraction modern radiocarbon >0.08, can be graphitized successfully. Samples smaller than 0.08mgC can be graphitized without any fractionation occurring, but radiocarbon measurements will not be accurate unless the AMS analysis of these samples can be optimised for such small current beams, which remains to be demonstrated.

Acknowledgements

We would like to thank James Rolfe for running the stable isotope measurements, as well as the Royal Society and NERC grant NE/L006421/1 for research support.

References

Delque-Kolic E., C. Souprayen, J. F. Tannau, B. Thellier, J. Vincent, I. Caffy, C. Comby- Zerbino, J. P. Dumoulin, S. Hain, M. Massault, C. Moreau, A. Quiles, and V. Setti. Advances in handling small radiocarbon samples at the Laboratoire de Mesure du Carbone 14 in Saclay, France. *Radiocarbon*, 55(2-3):648–656, 2013.

Le Clercq, M., Van Der Plicht, J., Gröning, M. New 14C reference materials with activities of 15 and 50 pMC. *Radiocarbon,* 40(1): 295-297, 1998

L. Rinyu, I. Futo, Å. Z. Kiss, M. Molnar, E. Svingor, G. Quarta, and L. Calcagnile. Performance test of a new graphite target production facility in ATOMKI *Radiocarbon*, 49(2): 217–224, 2007.

G. M. Santos, J. R. Southon, K. C. Druffel-Rodriguez, S. Griffin, and M. Mazon. Magnesium perchlorate as an alternative water trap in AMS graphite sample preparation: A report on sample preparation at KCCAMS at the University of California, Irvine. *Radiocarbon*, 46(1): 165–173, 2004.

G. M. Santos, R.B. Moore, J.R. Southon, S. Griffin, E. Hinger, and D. Zhang. AMS C-14 sample preparation at the KCCAMS/UCI facility: Status report and performance of small samples. *Radiocarbon*, 49(2): 255–269, 2007.

J. Turnbull, C. Prior, and Graphitization Workshop Participants. Report on the 20th International Radiocarbon Conference graphitization workshop. *Radiocarbon*, 52(3): 1230–1235, 2010.